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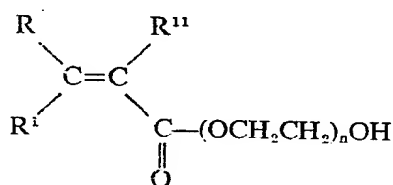
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 (72) Inventors MANFRED KREUDER HANS RUDOLPH,  
 KARL MERZ and WOLFGANG METZNER

(54) ESTERS OF SUBSTITUTED CINNAMIC ACID AND THEIR USE AS  
 U.V.-ABSORBERS

(71) We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The subject-matter of the present invention comprises compounds of the general formula



15 in which R represents a phenyl radical which may be substituted by halogen, alkyl, hydroxy or alkoxy radicals; R<sup>1</sup> stands for hydrogen, an alkyl, aralkyl or aryl radical; R<sup>11</sup> denotes CN or the radical COOR<sup>11</sup>; R<sup>11</sup> stands for an alkyl, aralkyl or aryl radical; and n represents the numbers 4—20,

as well as their production and their use for the protection of organic materials from U.V. radiation.

25 The alkyl, aralkyl, aryl or alkoxy radicals may be further substituted.

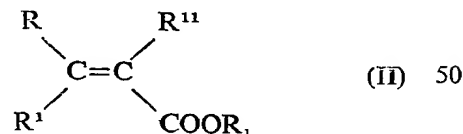
The radicals R are, for example, chlorophenyl, bromophenyl, methylphenyl, dimethylphenyl, ethylphenyl, butylphenyl, hydroxyphenyl, methoxyphenyl, ethoxyphenyl, butoxyphenyl. 30

The radicals R<sup>1</sup> besides hydrogen, are, for example, alkyl radicals with 1—12 carbon atoms, preferably those with 1—4 carbon atoms, such as CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>4</sub>H<sub>9</sub>, furthermore benzyl, phenylethyl and the radicals R. 35

The radicals R<sup>11</sup>, besides CN, are, for example, COOCH<sub>3</sub>, COOC<sub>2</sub>H<sub>5</sub>, COOC<sub>4</sub>H<sub>9</sub>, COO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H where n = 4—20, COOR where R has the same meaning as above, COOCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, COOCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>. 40

(I) Preferred compounds of the formula (I) are those in which R<sup>1</sup> stands for hydrogen and R<sup>11</sup> denotes CN or a carbalkoxy group with 1—4 carbon atoms in the alkoxy group. 45

The new compounds of the formula (I) can be obtained according to known processes, for example, by transesterification of compounds of the general formula



in which R, R<sup>1</sup> and R<sup>11</sup> have the same meaning as above, and

R<sub>1</sub> stands for an alkyl, aralkyl or aryl radical, with preferably equimolar amounts

of polyethylene glycols of the formula  $H(OCH_2CH_2)_nOH$  where  $n$  stands for the numbers 4—20, preferably in the presence of conventional esterification catalysts, such as, for example, tetrabutyl titanate or potassium carbonate, at temperatures of about 50 to about 150°C. The low-boiling alcohols such as e.g. methanol and ethanol, are distilled off in this operation and the transesterification product remains as the residue.

Compounds of the formula (II) are described, for example in German Patent Specification No. 1,103,136.

The starting compounds (II) are, for example,  $\alpha$ -cyano,  $\alpha$ -cyano-2-methoxy-,  $\alpha$ -cyano-2-ethoxy-,  $\alpha$ -cyano-4-hydroxy-,  $\alpha$ -cyano-4-methoxy-,  $\alpha$ -cyano-4-ethoxy-,  $\alpha$ -cyano-4-phenoxy-,  $\alpha$ -cyano-4-benzyloxy-,  $\alpha$ -cyano-4-(2-hydroxyethoxy)-,  $\alpha$ -cyano-2-chloro-4-hydroxy-,  $\alpha$ -cyano-2-chloro-4-methoxy-,  $\alpha$ -cyano-2-chloro-4-ethoxy-,  $\alpha$ -cyano-3-chloro-4-hydroxy-,  $\alpha$ -cyano-3-chloro-4-methoxy-,  $\alpha$ -cyano-3,5-dichloro-4-hydroxy-,  $\alpha$ -cyano-3-bromo-4-hydroxy-,  $\alpha$ -cyano-4-hydroxy-2-methyl-,  $\alpha$ -cyano-4-hydroxy-3-methyl-,  $\alpha$ -cyano-4-methoxy-3-methyl-,  $\alpha$ -cyano-2-ethoxy-3-methyl-,  $\alpha$ -cyano-2-methoxy-4-methyl-,  $\alpha$ -cyano- $\beta$ -methyl-2-methoxy-,  $\alpha$ -cyano- $\beta$ -methyl-2-ethoxy-,  $\alpha$ -cyano- $\beta$ -methyl-4-hydroxy-,  $\alpha$ -cyano- $\beta$ -methyl-4-methoxy-,  $\alpha$ -cyano- $\beta$ -methyl-4-phenoxy-,  $\alpha$ -cyano- $\beta$ -methyl-3-chloro-4-methoxy-,  $\alpha$ -cyano- $\beta$ -methyl-4-hydroxy-2-methyl-,  $\alpha$ -cyano- $\beta$ -ethyl-4-hydroxy-,  $\alpha$ -cyano- $\beta$ -ethyl-4-ethoxy-,  $\alpha$ -cyano- $\beta$ -ethyl-4-ethyl-4-isobutoxy-,  $\alpha$ -cyano- $\beta$ - $n$ -propyl-4-hydroxy-,  $\alpha$ -cyano- $\beta$ - $n$ -propyl-4-propoxy-cinnamic acid-methyl ester and the corresponding ethyl, propyl or butyl esters, 2-methoxy-4-methoxy-, 2-ethoxy-, 4-ethoxy-phenyl-methylene-malonate dimethyl ester and the corresponding diethyl, dipropyl or dibutyl esters.

The polyethylene glycols are, for example, tetraethylene glycol, hexaethylene glycol, octaethylene glycol or  $H(OCH_2CH_2)_nOH$ .

The compounds according to the invention are eminently suitable for protecting organic materials against u.v. radiation.

The compounds according to the invention are superior to the compounds described in German Patent Specification No. 1,103,136 in that, in addition to their very good u.v.-absorbing effect, they are excellently soluble or dispersible in water. Consequently, these substances are particularly suitable for application from aqueous bath, for example, for the protection of paper and cotton from u.v. radiation. Compared with the 2-hydroxy-benzophenones known as water-soluble u.v.-protective agents, the compounds according to the invention offer the advantage that the materials to be protected, such as e.g. paper or other

products of cellulose, are not attacked and not discoloured.

The compounds according to the invention are especially suitable for protecting natural substances, such as cotton, wood, paper or their conversion products, such as cellulose esters or nitrocellulose, for example, in the form of films, threads or fibres, against u.v. radiation. However, they are also suited for the protection of synthetic materials such as polyvinyl chloride, polyvinylidene chloride, polystyrene, polycarbonates, polyacrylates, alkyd resins, polyamides, polyethylene, polypropylene, polyesters and polyurethanes against u.v. radiation.

Application of the compounds according to the invention is carried out in known manner, for example, by mechanical incorporation in the materials to be protected. A preferred method of application is that from an aqueous suspension, optionally with the addition of emulsifiers, or from solutions in mixtures of water and organic solvents, for example water/alcohol or water/dioxan. The dispersions or solutions the concentration of which preferably lies at about 1—10 per cent by weight but may also amount to up to 20 per cent by weight, are applied in the usual way to the materials such as mouldings, foils or fabrics which are subsequently dried.

The materials finished with the compounds according to the invention are largely impervious to u.v. light and therefore ensure an excellent protection, for example, of substances which are sensitive to light, such as food, which are packed with these materials.

The compounds according to the invention can also be used with satisfactory results as cosmetic u.v.-protective agents, for example, in creams, oils and sprays for the protection against sun light.

Suitable compounds of the formula (I) are, for example;

$\alpha$ -cyano-4-methoxy-cinnamic acid-tetraethylene-glycol monoester,  $\alpha$ -cyano- $\beta$ -methyl-4-ethoxy-cinnamic acid-octaethylene-glycol monoester,  $\alpha$ -cyano-4-methyl-cinnamic acid-polyethylene glycol ( $n=20$ ) monoester,  $\alpha$ -cyano- $\beta$ -methyl-4-methoxy-cinnamic acid-tetraethylene glycol monoester,  $\alpha$ -cyano-2-chloro-4-ethoxy-cinnamic acid-octaethylene glycol monoester,  $\alpha$ -carbomethoxy-4-methoxy-cinnamic acid-hexamethylene glycol monoester,  $\alpha$ -carbo-ethoxy-4-methoxy-cinnamic acid-polyethylene glycol ( $n=20$ ) monoester,  $\alpha$ -carbomethoxy-cinnamic acid-octaethylene glycol,  $\alpha$ -carbo-ethoxy- $\beta$ -methyl-4-methoxy-cinnamic acid-tetraethylene glycol.

#### Example 1

(a) A mixture of 273 g  $\alpha$ -cyano- $\beta$ -

- 5 methyl-*p*-methoxy-cinnamic acid-*n*-butyl ester, 1000 g polyethylene glycol (average molecular weight 1000) and 4 g tetra-*n*-butyl titanate was heated at 140°C and 20 mm Hg for 2 hours. As reaction product there was obtained a soft substance with an iodine number (30% in toluene) of 40—50 and an n.v. absorption maximum in methanol of 321 nm ( $\epsilon = 10,200$ ).
- 10 (b) 231 g  $\alpha$ -cyano- $\beta$ -methyl-*p*-methoxy-cinnamic acid methyl ester, 400 g polyethylene glycol (average molecular weight 400) and 4 g tetra-*n*-butyl titanate were heated at 145°C and 10 mm Hg for 1½ hours. The resultant viscous oil has an iodine number (30% in toluene) of 30—40 and an u.v. absorption maximum in methanol at 320 nm ( $\epsilon = 11,000$ ).
- 15 (c) 139 g methoxyphenyl-methylene-malonic acid diethyl ester, 200 g polyethylene glycol (average molecular weight 400) and 5 g potassium carbonate were stirred at 60°C and 10 mm Hg for 2½ hours; 23 g ethanol were distilled off. After filtering off with suction from the catalyst, there were obtained 316 g of an oil with an iodine number (30% in toluene) of 10 and an u.v. absorption maximum at 311 nm ( $\epsilon = 24,000$ ).
- 20
- 25
- 30
- 35
- 40
- 45

#### Example 2

Transparent paper was dipped into 1% aqueous solutions of the u.v. absorbers mentioned in the following Table, squeezed between glass rods, dried, calendered, and illuminated in a xenon test apparatus for 100 hours. The stability of the u.v. absorber was tested as follows: the paper sample containing the u.v. absorber is placed on a paper containing an optical brightening agent. As long as the u.v. absorber is intact, illumination with u.v. light makes the bottom paper appear dark, but as soon as the u.v. absorber is destroyed, the bottom paper begins to fluoresce.

U.v. absorber		Appearance of paper before after illumination		Stability of u.v. absorber
50	1. nil	white	white	—
	2. $\alpha$ -cyano- $\beta$ -methyl- <i>p</i> -methoxy-cinnamic acid-dodeca-ethylene glycol-monocster	white	white	good
55	3. $\alpha$ -cyano- <i>p</i> -ethoxy-cinnamic acid-octa-ethylene glycol-monoester	white	white	good
60	4. 2-hydroxy-4-methoxy-benzophenone-5-sulphonic acid	yellowish	pale yellow	not so good
65	5. 2,2'-dihydroxy-4,4'-dimethoxy-benzophenone-5-sulphonic acid sodium salt	pale yellow	brownish	not so good

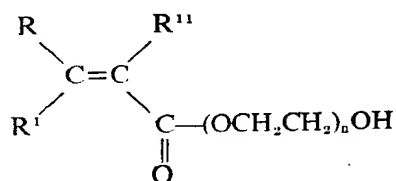
#### Example 3

Pergamylene paper was treated as in Example 2 and subsequently exposed to daylight for 100 hours. The following results were obtained (the stability was tested according to the process of Example 2):

U.v. absorber		Appearance of paper before after illumination		Stability of u.v. absorber
1.	nil	white	white	—
5	2. $\alpha$ -cyano- $\beta$ -methyl- <i>p</i> -methoxy-cinnamic acid-hexa-ethylene glycol-monoester	white	white	good
10	3. $\alpha$ -cyano- <i>p</i> -methoxy-cinnamic acid-octa-ethylene glycol-monoester	white	white	good
15	4. 2-hydroxy-4-methoxy-benzophenone-5-sulphonic acid	yellowish	yellowish	spotty, low u.v. absorption
20	5. 2,2'-dihydroxy-4,4'-dimethoxy-benzophenone-5-sulphonic acid sodium salt	pale yellow	pale yellow	spotty, low u.v. absorption

## WHAT WE CLAIM IS:—

1. Compounds of the formula



in which

25 R represents a phenyl radical which may carry at least one substituent selected from halogen, alkyl, hydroxy and alkoxy radicals,

30 R<sup>1</sup> represents a hydrogen atom or an alkyl, aralkyl or aryl radical,

R<sup>11</sup> represents CN or the radical COOR<sup>111</sup> wherein R<sup>111</sup> represents an alkyl, aralkyl or aryl radical,

35 and n represents an integer from 4 to 20, any of the aforesaid alkyl, aralkyl, aryl or alkoxy radicals being optionally substituted.

40 2. Compounds according to claim 1 in which R is a chlorophenyl, bromophenyl, methylphenyl, dimethylphenyl, ethylphenyl, butylphenyl, hydroxyphenyl, methoxyphenyl, ethoxyphenyl or butoxyphenyl radical.

3. Compounds according to claim 1 or 2 in which R<sup>1</sup> is hydrogen.

45 4. Compounds according to claim 1 or 2 in which R<sup>1</sup> is an alkyl group of 1 to 12 carbon atoms, benzyl, phenylethyl or a phenyl radical which may carry at least one substituent selected from halogen, alkyl, hydroxy and alkoxy radicals, the alkyl and al-

koxy radicals optionally carrying substituents.

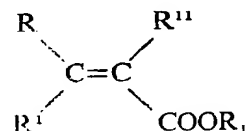
5. Compounds according to claim 4 in which R<sup>1</sup> is an alkyl group of 1 to 4 carbon atoms.

6. Compounds according to any of claims 1 to 5 in which R<sup>11</sup> is CN or a carboxy radical having 1 to 4 carbon atoms in the alkoxy group.

7. Compounds according to any of claims 1 to 5 in which R<sup>11</sup> is COO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H wherein n is an integer from 4 to 20, COOCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, COOCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> or COOR wherein R is a phenyl radical which may carry at least one substituent selected from halogen, alkyl, hydroxy and alkoxy radicals, the alkyl and alkoxy radicals optionally carrying substituents.

8. Each of the compounds according to claim 1 which are specifically mentioned herein.

9. A process for the production of compounds according to any of claims 1 to 8 in which a compound of the formula



wherein R, R<sup>1</sup> and R<sup>11</sup> have the meanings given in claim 1 and R<sub>1</sub> represents an alkyl, aralkyl or aryl radical, is reacted with a polyethylene glycol of the formula H(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH wherein n is an integer of 4 to 20.

10. A process according to claim 9 in

which the reaction is effected at 50°C to 150°C.

11. A process according to claim 9 or 10 in which the compound of formula (II) and the polyethylene glycol are used in equimolar quantities.

12. A process according to any of claims 9, 10 or 11 in which the reaction is carried out in the presence of an esterification catalyst.

13. A process according to claim 12 in which the catalyst is tetrabutyl titanate or potassium carbonate.

14. A process for the production of compounds according to claim 1 substantially as hereinbefore described in Example 1.

15. Compounds according to claim 1 whenever prepared by a process according to any of claims 9 to 14.

16. A composition resistant to the effects of ultra-violet radiation which comprises an organic material having incorporated therein as an ultra-violet absorber a compound according to any of claims 1 to 8 or 15.

17. A composition according to claim 16 in which the organic material is cotton, wood, paper, a cellulose ester, nitrocellulose or a synthetic polymer.

18. A composition according to claim 17 in which the organic material is a synthetic polymer selected from polyvinyl chloride, polyvinylidene chloride, polystyrene, polycarbonates, polyacrylates, alkyd resins, poly-

amides, polypropylene, polyesters and polyurethanes.

19. A process for producing a material which is resistant to the effects of ultra-violet light which comprises incorporating into an organic material, as an ultra-violet absorber, a compound according to any of claims 1 to 8 or 15.

20. A process according to claim 19 which comprises applying to the organic material an aqueous suspension or solution of the ultra-violet absorber and subsequently drying the organic material.

21. A process according to claim 20 in which the aqueous solution or suspension contains up to 20% by weight of the ultra-violet absorber.

22. A process according to claim 21 in which the aqueous solution or suspension contains 1 to 10% by weight of the ultra-violet absorber.

23. A process according to claim 19 substantially as hereinbefore described in Example 2 or 3.

24. Materials resistant to the effects of ultra-violet light whenever produced by a process according to any of claims 19 to 23.

For the Applicants,  
CARPMAELS & RANSFORD,  
Chartered Patent Agents,  
24, Southampton Buildings,  
Chancery Lane, W.C.2.

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